PREPARATION OF SILICON CARBIDE WHISKER REINFORCED SILVER COMPOSITE MATERIAL IN A WEIGHTLESS ENVIRONMENT SKYLAB EXPERIMENT M561

By

Tomoyoski Kawada
(Principal Investigator)
Sennosuke Takahaski*, Susumu Yoshida,
Eiichi Ozaqa and Renpei Yoda
National Research Institute for Metals
2-3-12, Nakameguro, Meguro-ku, TOKYO

SUMMARY

The object of the experiment was to get Ag and SiC whisker composites with high density and uniform distribution of whiskers by heating and pressurizing sintered products above the melting point of Ag in a weightless environment.

This report describes the results of the examination carried out on the samples processed on Skylab and comparison with those prepared on the ground. The SiC nominal volume fraction is 2, 5, and 10%. The size of each sample is 8mm in diameter and about 30mm in length. The microhardness is measured on a longitudinal section of the sample. Also the distribution density of whiskers is estimated by observing the section under an optical mocroscope. The difference between the Skylab samples from the ground based test samples is clearly revealed in the uniform distribution of hardness values and the nonexistence of any floating whiskers.

INTRODUCTION

Composite materials of metallic matrix reinforced by high-strength whiskers such as SiC and Al_2O_3 have been attracting much attention as promising candidates for high-strength materials. At present, however, their practical application has not been realized. The greatest trouble in processing such whisker composite materials is that it is difficult to obtain sufficiently high-density material by applying the usual powder metallurgical techniques of mixing, compacting and sintering.

As for a method to cope with this difficulty, it may be expected that a process of melting and pressurizing the metal matrix is effective for raising the density of the product in processing such materials. Unfortunately, there is a possibility that the mixture might separate into

*Paper presented by Sennosuke Takahaski

two components, i.e., metal and whiskers, as soon as the metal matrix is melted down, and lose its unity as a composite material, because the specific gravity of the whisker is generally lower than that of the matrix.

If in a weightless environment such as on Skylab a metal-whisker composite which is prepared by the conventional powder metallurgical technique is kept in a molten state, it would be possible to obtain a homogeneous composite material, because there is no influence of buoyancy and thermal convection in a weightless environment. But by the melting process only, it will be impossible to raise the density of the composite by removing voids further than that of the sintered state. Therefore, one of the points of our proposal was laid in a procedure to positively remove voids by pressurizing the sample during melting.

The present report describes the result of comparative evaluation on the samples of SiC whisker reinforced Ag composite material processed on Skylab and those processed on the ground under otherwise similar conditions. The experiment was carried out following the line of the above-stated idea.

The samples and the ampoules containing them were designed and prepared by NRIM and the cartridges containing the ampoules by Westinghouse Astronuclear Laboratory. The coordination of the experiment was performed by MSFC.

The melting experiments on Skylab were carried out twice, the first in the SL-3 mission in September 1973 and the second in the SL-4 mission in December 1973. In this report the results are described for the samples processed during the SL-3 mission.

PREPARATION OF SAMPLES

The selection of materials for the experiment was done bearing in mind the following:

1) the temperature range of the multipurpose electric furnace to be used in this experiment,
2) the significant difference in the specific gravity between the whisker material and the matrix metal,
3) there was to be little chemical reaction between the whisker material and the metal matrix,
4) the need for easy availability of the materials which are well controlled in their particle size and shape.

After the screening of some materials, silver of m.p. 961°C and specific gravity 9.4 at molten state was selected as the matrix and silicon carbide (SiC) whiskers of specific gravity 3.1 as the reinforcing material. The particle size of fine powder of silver used was under

0.5 μm in diameter. The SiC whiskers used were about 0.1 μm in diameter on average and 10μm in length on average.

In a preliminary measurement the contact angle between Ag and bulk SiC crystal turned out to be about 120°. Any significant reaction as observed in the interface between SiC and molten Cu was not shown in the case of SiC and molten Ag.

SiC whiskers of 2, 5, and 10 volume % were mixed in Ag powder. Before mixing they were coated with Ag. Cylindrical green samples of 8mmϕ in diameter and about 35mm in length were prepared by well mixing the shiskers and Ag powder, compacting the mixture in a press, sintering it at about 900°C in a hydrogen gas atmosphere and finally hot-pressing it lightly.

Figure 1 shows the ampoule that contained the sample. The ampoule assembly consisted of a silica tube, a graphite sheath, a piston rod of graphite and silica and a coiled spring for pressurizing the sample from one end. The spring was made of special heat-resistant alloy. The applied force by the spring was adjusted to about 30kg in the initial condition before melting. The pressurizing mechanism was designed so as to crush voids in the material in molten state by hydrostatic pressure applied to the sample. Now let us assume that the whiskers are uniformly and unidirectionally arranged in a state of the closest packing and that the molten metal with a surface tension γ forms a contact angle Θ with the whiskers. The pressure P which is necessary to crush voids between the whiskers is given by the following equation,

$$P = \frac{-2\gamma v \cos\Theta}{r}$$

where r is the radius of the whisker and v is its volume fraction. For example, if it is assumed that r=0.05μm, Θ=120°, γ=890dyne/cm and v=0.1 in the above equation, P turns out to be 18kg/cm.

EXPERIMENTAL PROCEDURE

The sample ampoule was loaded and sealed into the cartridge made of stainless steel. Three sample ampoules were set together in the multipurpose electric furnace and heat treatment was performed under a prescribed condition.

1) Skylab experiment

Figure 2 shows the temperature profile during processing of the Skylab samples. As shown in the figure, the samples were heated at the maximum heat leveler temperature of 1010°C for about 4 hrs and then cooled in the switched-off furnace. It was estimated from the results of the ground-based tests that the measured temperature was about 20°C higher than that at the center of the sample. Accordingly, the temperature of the samples is thought to have been kept above the melting point of Ag for about 5 hrs.

2) Ground-based experiment

In the ground-based experiment the samples were heated and cooled in a furnace that was quite similar to the multipurpose electric furnace on Skylab. The sample axes were held in the vertical position and their spring ends were kept downward. Table I shows the maximum heating temperature and the soaking time at that temperature. Experiments under different conditions with the maximum temperatures of 980°C and 985°C were also carried out. But the samples for these experiments are not evaluated in this report because the metal matrix did not seem to have attained a sufficiently molten state in these cases.

EVALUATION OF SAMPLES

The evaluation tests were carried out for six samples shown in Table I, three for the Skylab test and the other three for the ground-based test (GBT).

1) X-ray radiography

X-ray radiographs were taken on the samples at NASA-MSFC with the cartridges unopened. Examples are shown for the Skylab sample 1A′ and the GBT sample 5A in Figure 3(a), (b), respectively. It was recognized that the piston mechanism in the ampoule had worked without trouble. But it was presumed that relaxation in the applied pressure had occurred to some extent during heating as some permanent deformation was observed in the coiled spring at its higher temperature end.

2) Macroscopic appearance

Figure 4 (a), (b) show macroscopic appearances of the samples. The samples 1A′ and 1B′ were contaminated with graphite from the graphite sheath at their bottom sides. This contamination is thought to be due to the fact that the temperature of the furnace was a little too high (1010°C). There was observed some flowed out material due to a crack in the graphite sheath in 1C′ sample as shown in Figure 4. At the bottom side of the GBT samples was recognized a tarnished zone. This shows that floating and coagulating of whiskers occurred during melting at the bottom side of the GBT samples.

3) Measurement of bulk density

The bulk density of the samples was measured for each sample both before and after the experiment. The density ratio was determined from the bulk density. Here the density ratio means the ratio of the bulk density to the ideal theoretical density.

Table II shows the weight, size, and density ratio of the samples. The density ratio of the Skylab samples 1A′ and 1B′ was 3 and 5% larger than that of the green samples, respectively.

A decrease of 2% in the density ratio was measured for the Skylab sample 1C′. As already described, some material flowed out in this sample

through a crack in the graphite sheath. The sheaths of 1A′ and 1B′ samples were not broken, but their weights decreased by about 1.3 g. It was perhaps due to loss of material by penetration of molten material through the graphite sheaths. For the GBT samples 5A and 5B a decrease of a small amount of weight was measured.

4) Macrostructural observation

Each sample was cut longitudinally at about one half of the radius off the center axis as shown in Figure 5. The cut section was polished and used for measurements.

Figure 6(a), (b) show the macrostructure revealed on the section. A considerable number of voids were observed on every section. In every Skylab sample, a transversal zone where voids diminished was observed. It corresponded to a region which bounded the graphite contaminated part (cf. Figure 4). It seems that the occurrence of this zone depended on the temperature distribution in the sample during melting.

5) Microstructure and measurement of distribution density of whiskers

Figure 7(a), (b) show the microstructures at both ends, the spring side and bottom side, of the sections. There is observed a difference in the void distribution between the Skylab Samples and the GBT ones. For the GBT samples 5A and 5B there were more voids at the bottom end, i.e., the upside of the sample, than at the spring end. For the Skylab samples no such difference in void density between both ends was observed and the voids themselves were generally less than for the GBT samples.

The same situation was observed for sample 5C but at its bottom end was seen a layer of 0.1mm in thickness, which was thought to be the result of exudation of metal. Those voids found at the bottom end of GBT samples are considered to be the traces of whiskers which fell off the metal matrix after floating up and coagulating during melting.

Figure 8 (a), (b) show photomicrographs of a large magnification of the section. Using these photographs the distribution density of whickers was measured by counting the spots which appeared to be whisker sections. In this case the counted numbers of whiskers depended on the resolving power in the microscope and photographic conditions, because the diameters of whiskers varied over a wide range around the mean diameter of 0.1um. Accordingly, these measured distribution densities are to be regarded only to indicate relative values.

Figure 9 (a), (b) show the distribution density of whiskers for the Skylab sample 1A and the GBT sample 5A. In the measurement of the distribution density, mocrophotographs were taken at several positions as shown in Figure 5. The dimension of a region taken on one photograph was $85 \times 60 \mu m^2$. In each region three squares of $20 \times 20 \mu m^2$ were picked up at random. The number of whiskers contained in the square was counted and the distribution density was calculated. The average value and the standard deviation were calculated for each three values corresponding to each position on the sample section in Figure 9. The left side origin of the abscissa in Figure 9 corresponds to the spring end of the sample.

These values have only a relative meaning as mentioned above. However, the following could be said from the comparison of the result for 1A′ with that for 5A:
no significant difference in the scatter in the distribution density is noticed between 1A′ and 5A; the density for 1A′ is generally a little larger than that for 5A; the density for 5A decreases towards the bottom end along the axial direction, but no such tendency is observed for 1A′. For B and C samples, reliable measurement of the distribution density could not be made because of large volume fractions of whiskers.

6) Measurement of microhardness

Figures 10 (a), (b), 11 (a), (b), and 12 (a), (b) show the microhardness of the samples. The measurement of hardness was carried out by a microvickers hardness tester with a load of 100g. Measured positions are shown in Figure 5. At each position the hardness was measured on five points at intervals of about 500μm. The mean values and the standard deviations were calculated for each five hardness numbers and plotted in figures 10, 11, and 12 corresponding to the positions on the section. The origin of the abscissa of the figures corresponds to the spring end of the sample.

The hardness for the Skylab samples showed a tendency of smaller change with position than for the GBT samples. To examine in more detail the change of hardness with position, the microhardness for the Skylab sample 1A′ and the GBT sample 5A was measured at 2mm intervals in the longitudinal direction and at 200μm intervals in the transversal direction. The results are shown in Figure 13 (a), (b). These histograms show the following trends:
the median value of the hardness number is apparently higher for 1A′ than for 5A; its fluctuation along the longitudinal direction is larger and oscillatory for 5A as compared with 1A′; the scatter of the hardness number on the same longitudinal positions is on the whole larger for 5A than for 1A′.

CONCLUSIONS

A melting experiment was carried out on Skylab for a sintered composite material consisting of a Ag matrix reinforced by SiC whiskers of 2 to 10 volume percent. The ampoule containing the sample was equipped with a device to pressurize the sample during melting.

Melting experiments were also performed on the ground under otherwise similar conditions. The products processed on Skylab and on the ground were subjected to comparative evaluation and the following conclusions were obtained:
1) An increase in the density ration was obtained by melting and pressurizing. The degree of increase was approximately the same for the Skylab and the GBT samples.

2) Floating and coagulation of whiskers were observed at the upside end of the GBT samples. The GBT samples showed a decreasing tendency in the distribution density of whiskers towards the upside end. No such phenomena were observed for Skylab samples.
3) The microhardness was generally smaller for the GBT samples than for the Skylab samples and showed large fluctuations along the axial direction as compared with the Skylab samples.
4) The above results are considered to indicate clearly the influence of buoyancy and thermal convection in the melted GBT samples, while the Skylab samples were devoid of such influence since they were processed in a weightless environment.

TABLE I. COMPOSITION OF SAMPLES AND SOAKING CONDITION

Sample		Volume Fraction of Whisker (%)	Maximum Heating Temperature (C)	Soaking Time (hrs)
Skylab Sample	1A′	2	1010	4
	1B′	5		
	1C′	10		
GBT Sample	5A	2	990	2.5
	5B	5		
	5C	10		

TABLE II. DENSITY RATIO OF SAMPLES BEFORE AND AFTER EXPERIMENT

Sample		Weight (g)		Length (mm)		Dia-meter (mm)	Density Ratio (%)	
		green material	after test	green material	after test		green material	after test
Skylab Samples	1A′	15.99	14.70	33.4	31.4	8	92	95
	1B′	14.61	13.29	33.7	31.0	8	87	92
	1C′	14.17	12.47	32.4	28.0	8	89	87
GBT Samples	5A	14.32	13.98	35.0	31.0	8	81	89
	5B	13.82	13.57	35.0	34.4	8	79	85
	5C	11.76	11.76	32.4	31.2	8	74	84

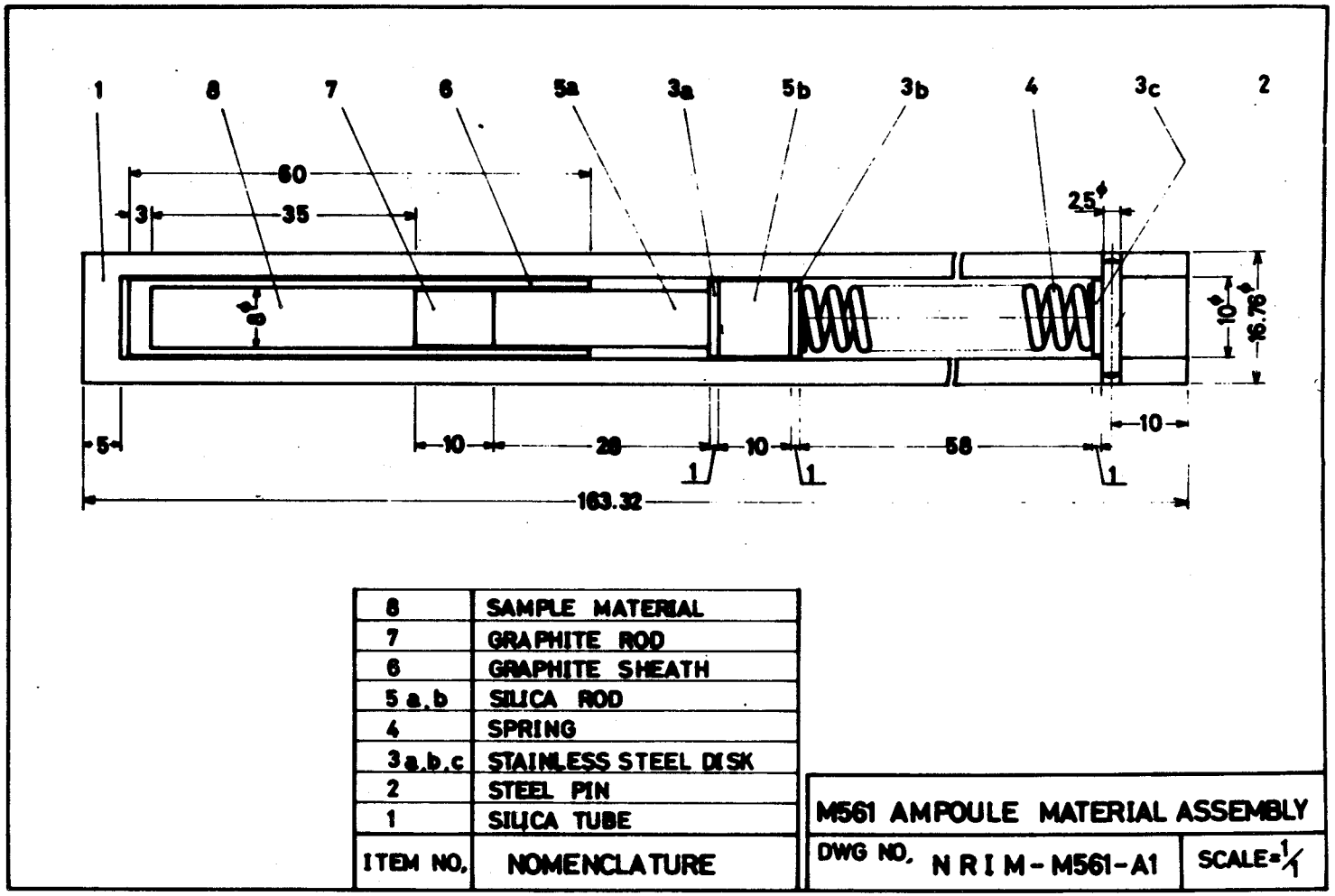


FIGURE 1. CROSS SECTION OF SAMPLE AMPOULE

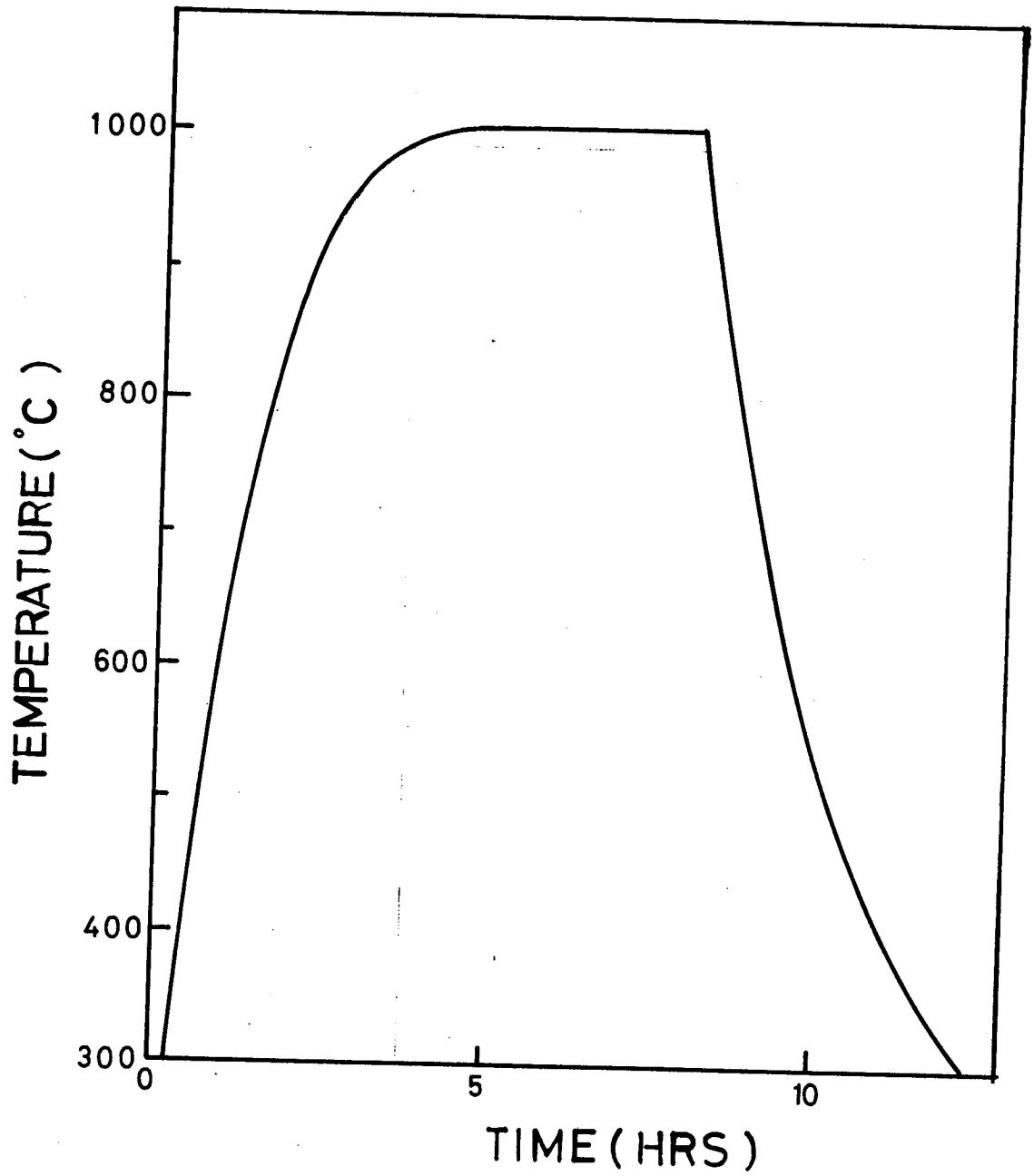


FIGURE 2. TEMPERATURE PROFILE DURING PROCESSING OF SKYLAB SAMPLES

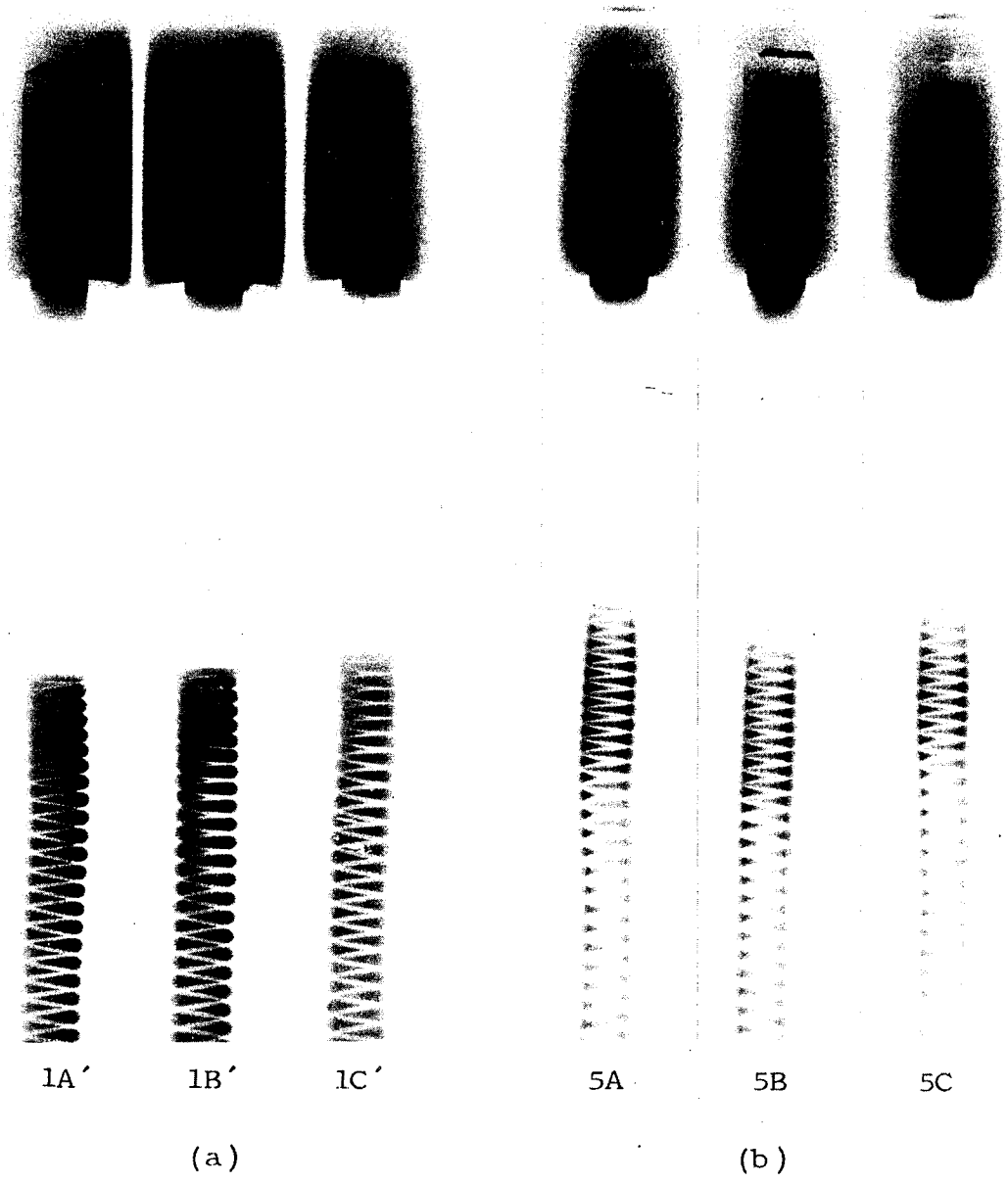


FIGURE 3. X-RAY RADIOGRAPHS, SKYLAB SAMPLES 1A´, 1B´, 1C´, (a) AND GBT SAMPLES 5A, 5B, 5C (b)

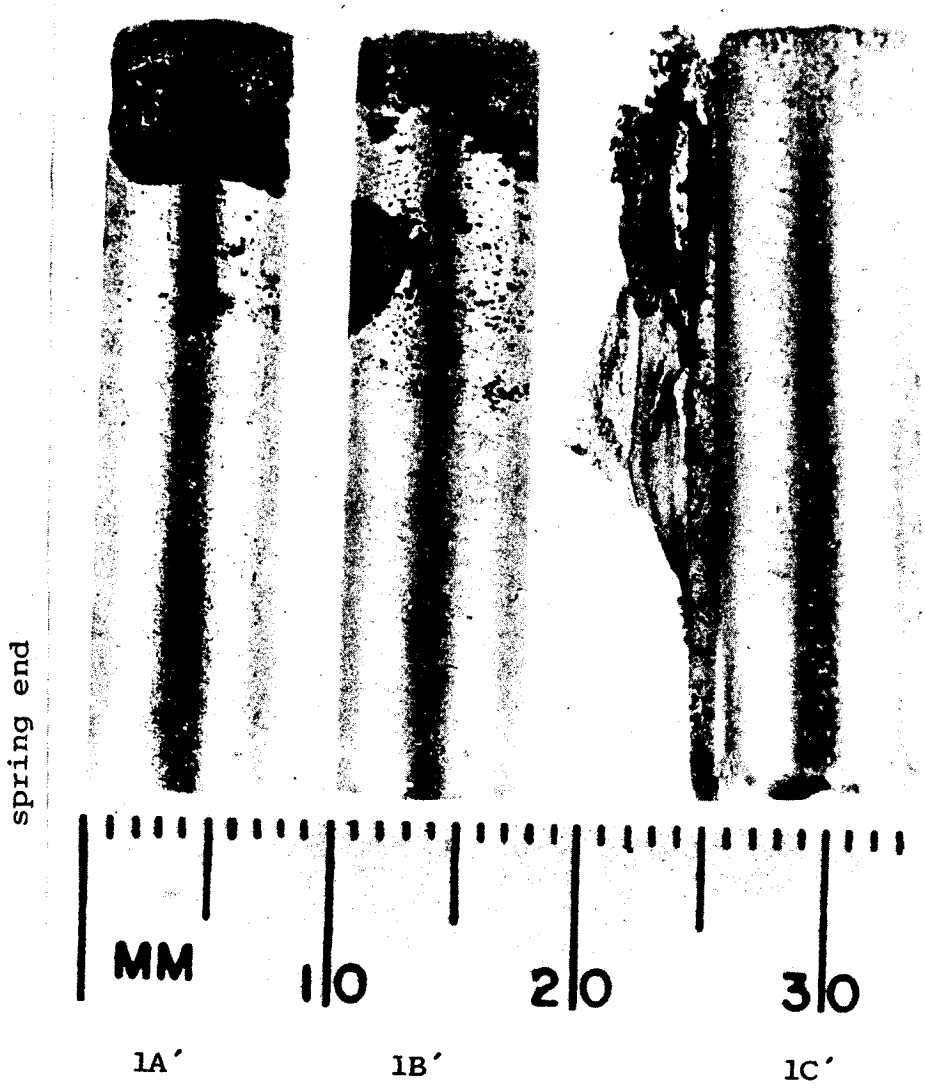


FIGURE 4A. MACROSCOPIC APPEARANCE OF SKYLAB SAMPLES 1A′, 1B′, AND 1C′

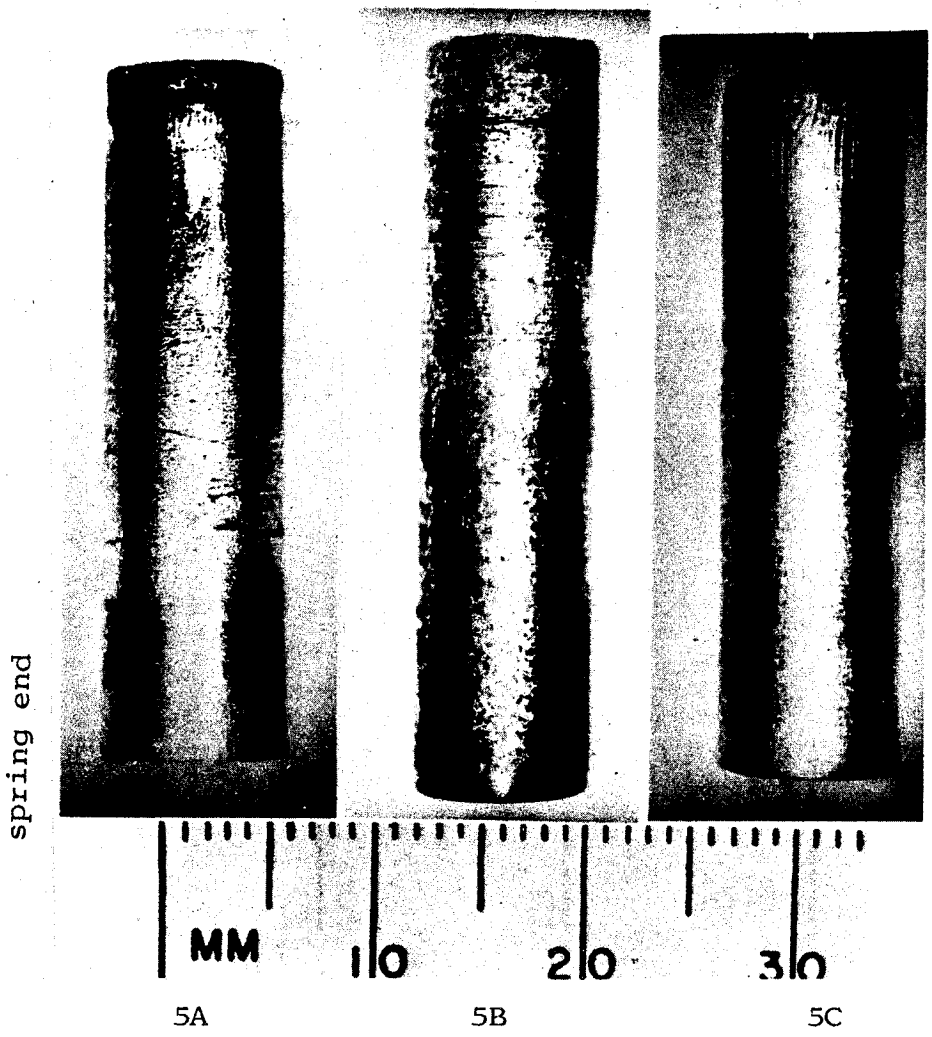


FIGURE 4B. MACROSCOPIC APPEARANCE OF GBT SAMPLES 5A, 5B, AND 5C

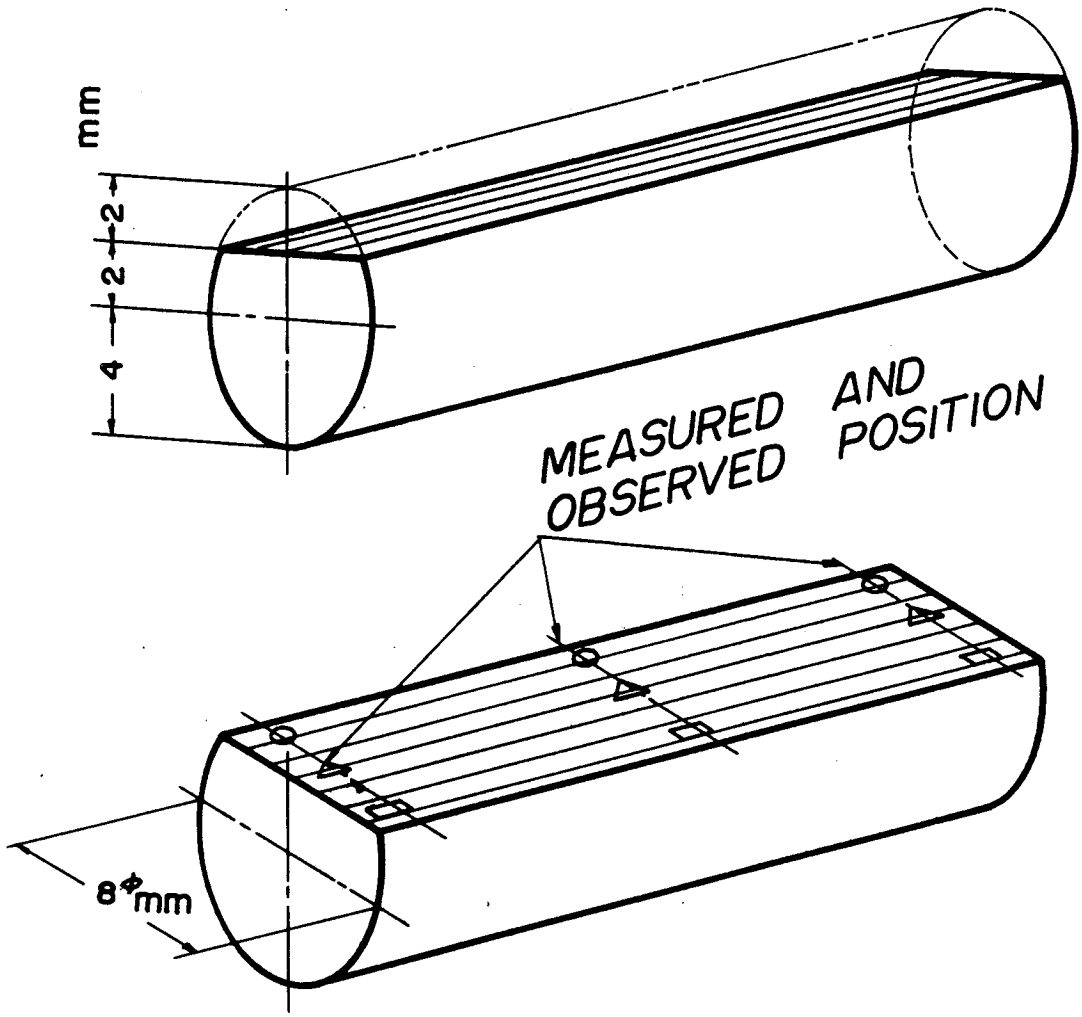


FIGURE 5. SCHEMATIC DIAGRAM OF CUT SECTION

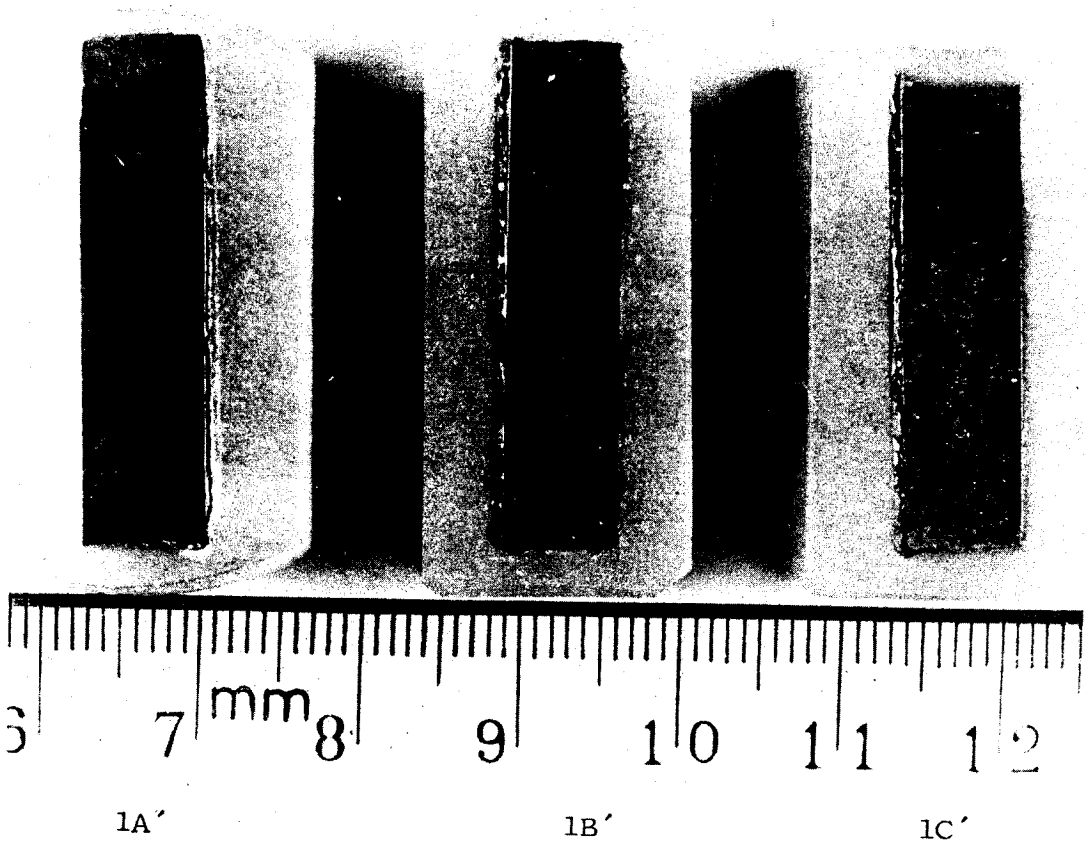


FIGURE 6A. PHOTOGRAPHS SHOWING MACROSTRUCTURE ON THE SKYLAB SAMPLES 1A′, 1B′, AND 1C′

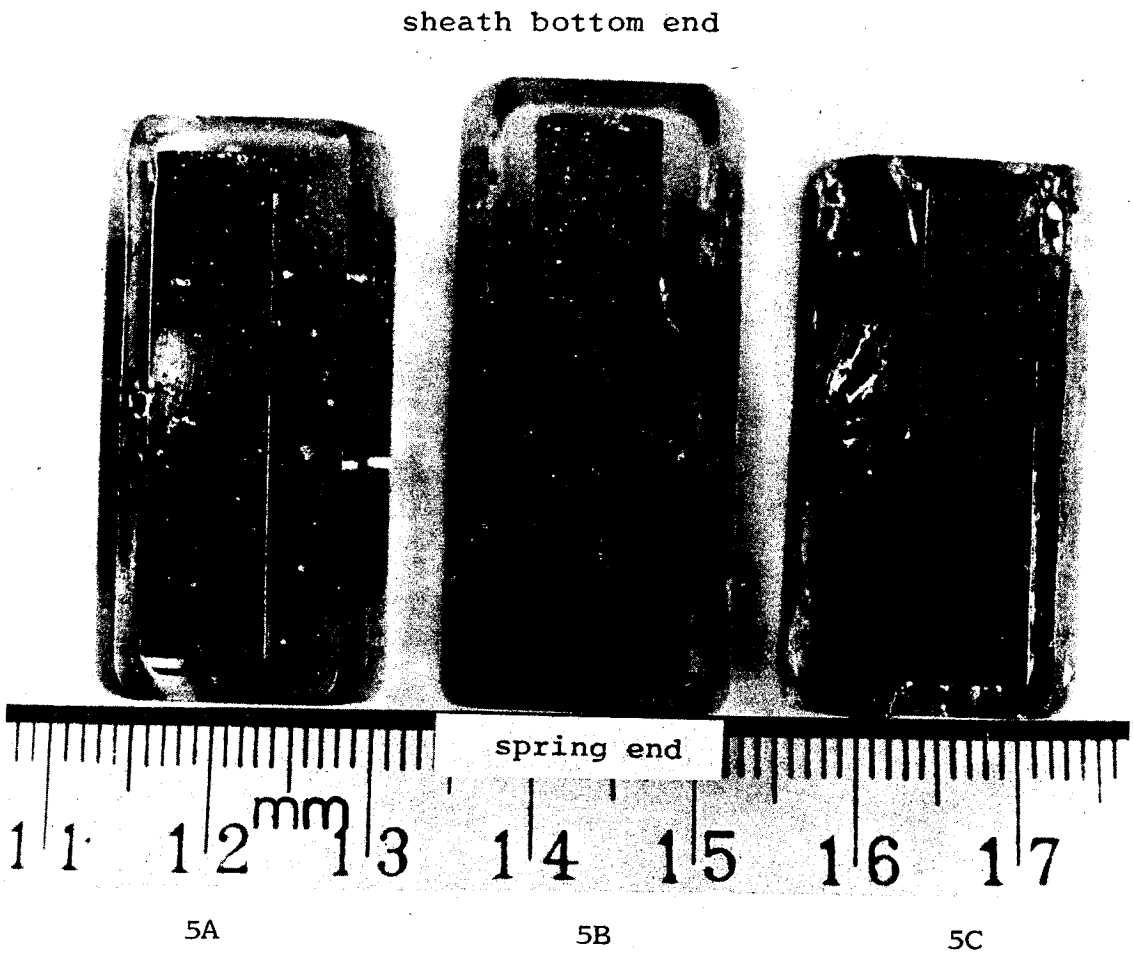


FIGURE 6B. PHOTOGRAPHS SHOWING MACROSTRUCTURE ON THE GBT SAMPLES 5A, 5B, AND 5C

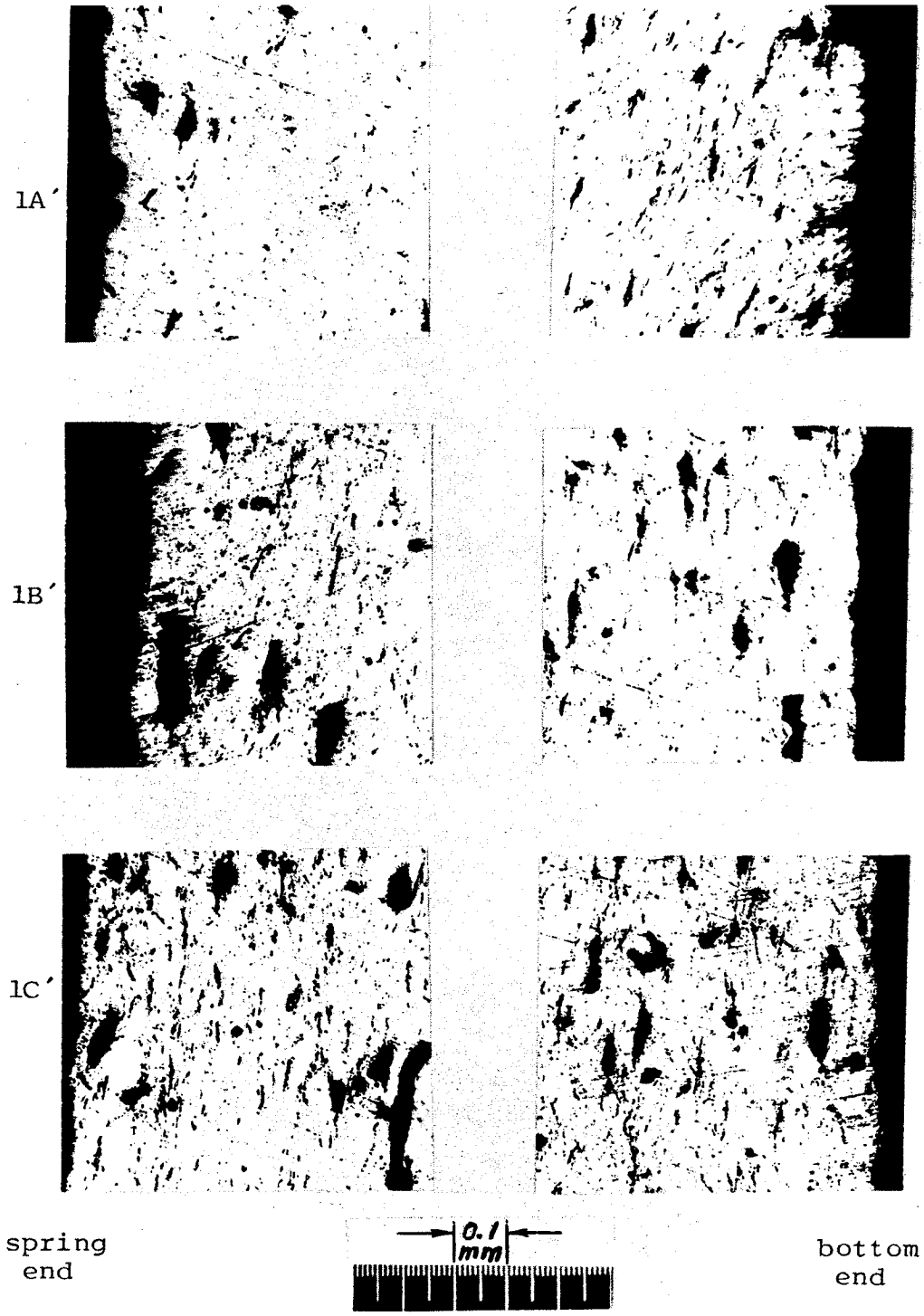


FIGURE 7A. PHOTOMICROGRAPHS SHOWING MICROSTRUCTURE AT THE SPRING END AND THE BOTTOM END, SKYLAB SAMPLES 1A′, 1B′, AND 1C′

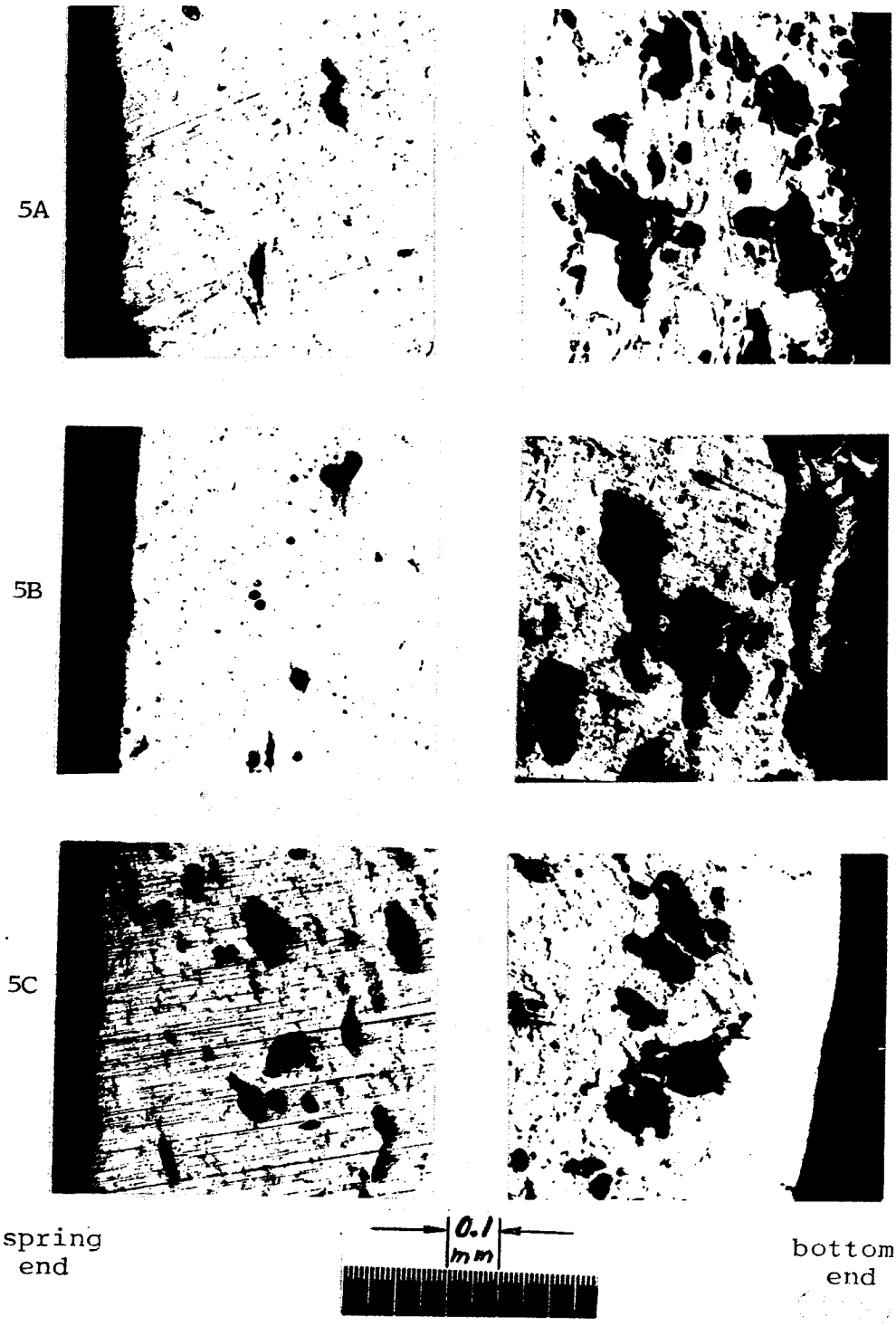


FIGURE 7B. PHOTOMICROGRAPHS SHOWING MICROSTRUCTURE AT THE SPRING END AND THE BOTTOM END, GBT SAMPLES 5A, 5B, AND 5C

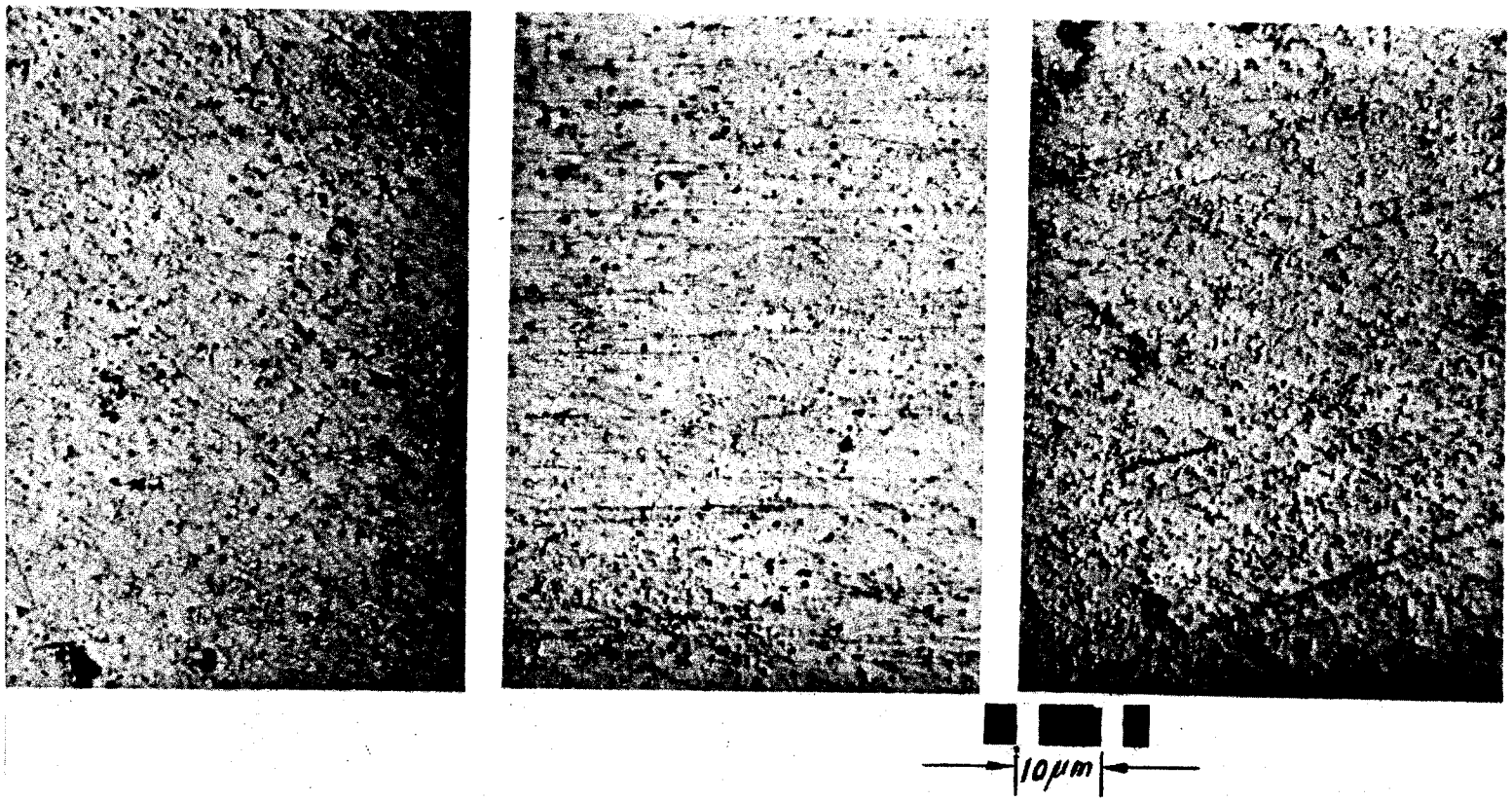
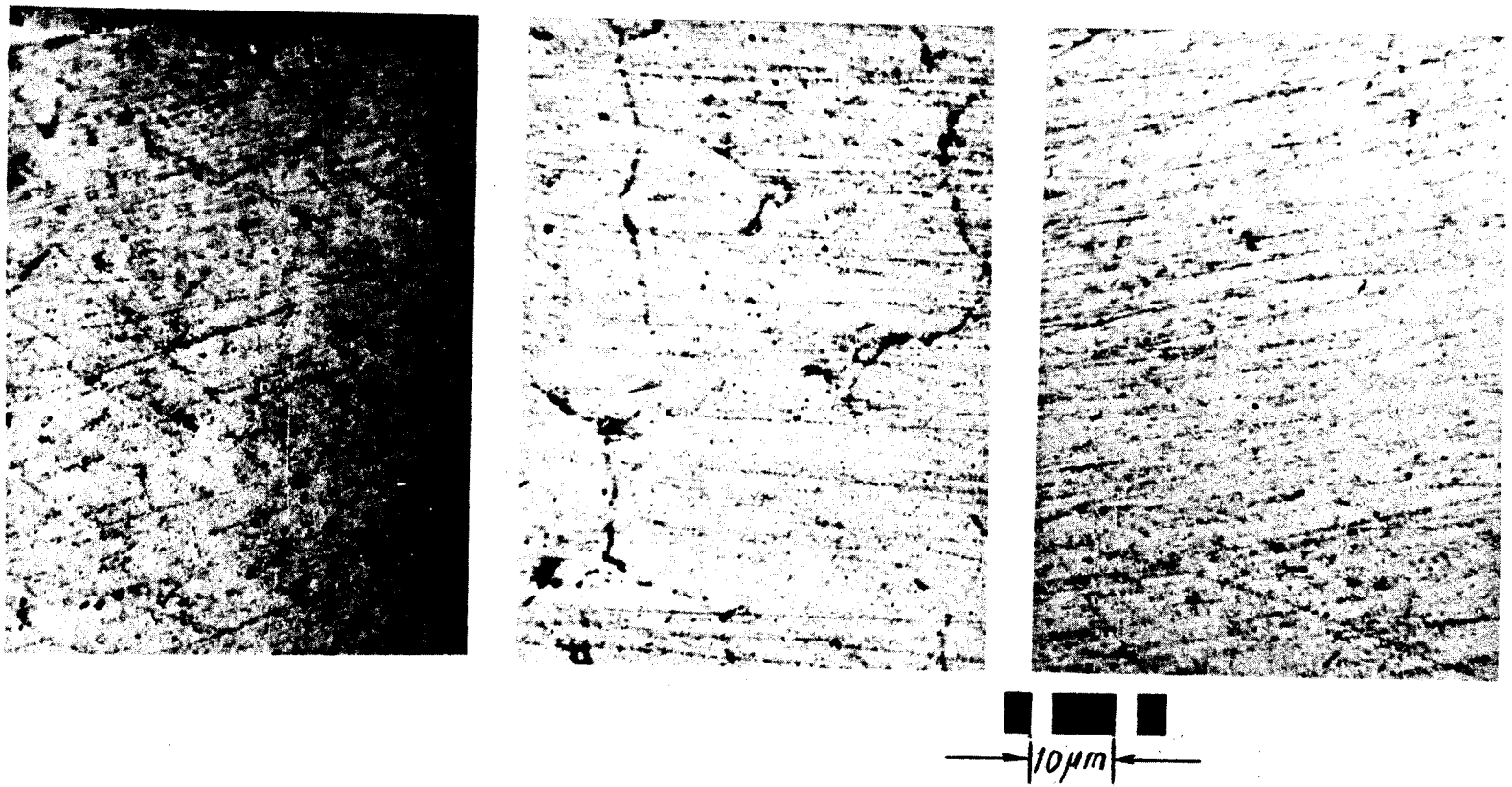


FIGURE 8A. PHOTOMICROGRAPHS SHOWING THE WHISKER DISTRIBUTION, SKYLAB SAMPLE 1A′



spring end

center

bottom end

FIGURE 8B. PHOTOMICROGRAPHS SHOWING THE WHISKER DISTRIBUTION, GBT SAMPLE 5A

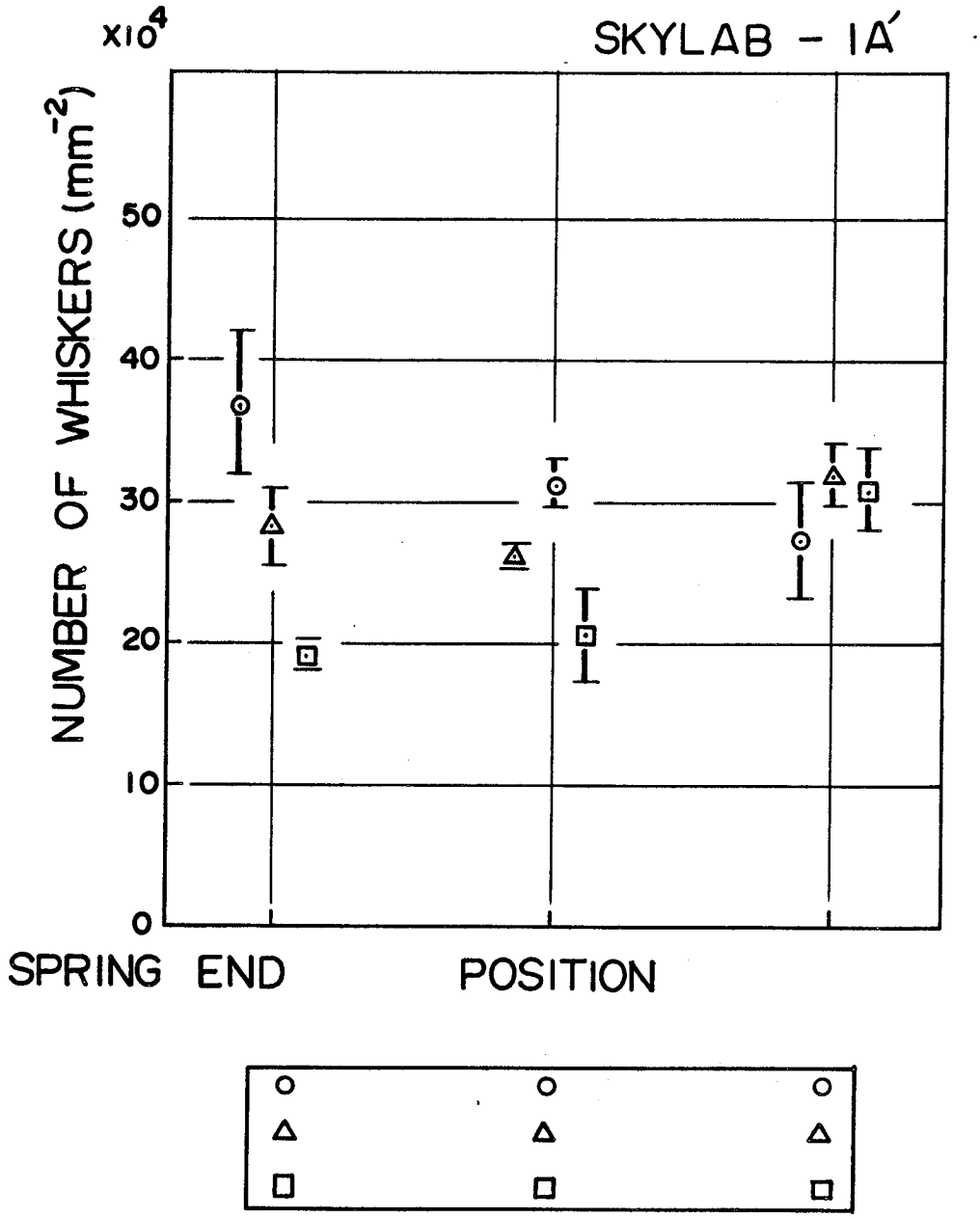
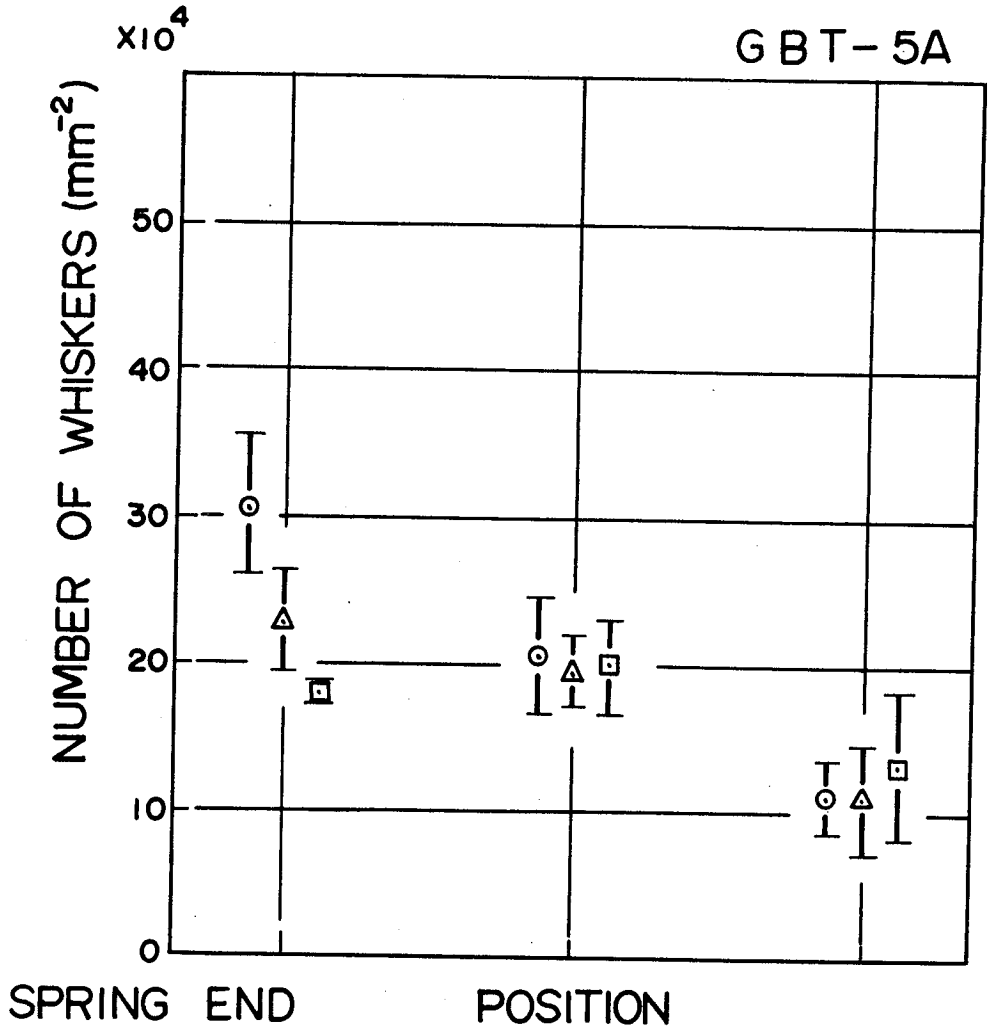


FIGURE 9A. DISTRIBUTION DENSITY OF WHISKERS, SKYLAB SAMPLE 1A'



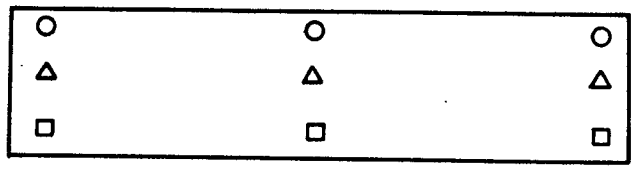
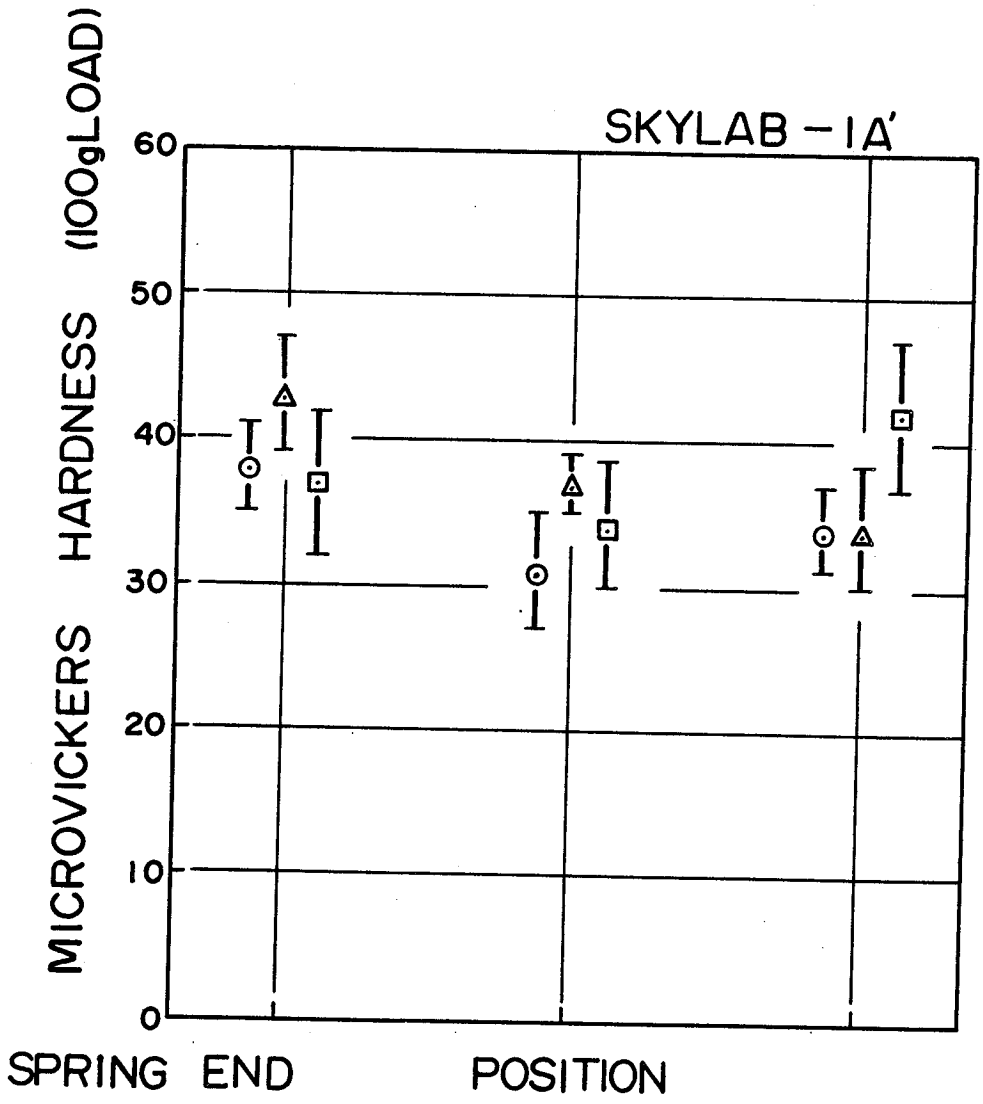


FIGURE 9B. DISTRIBUTION DENSITY OF WHISKERS
GBT SAMPLE 5A



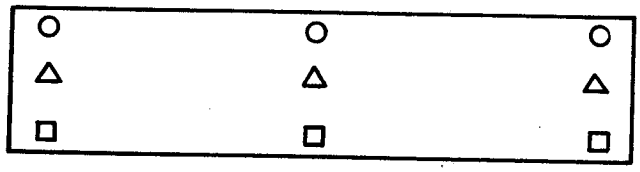
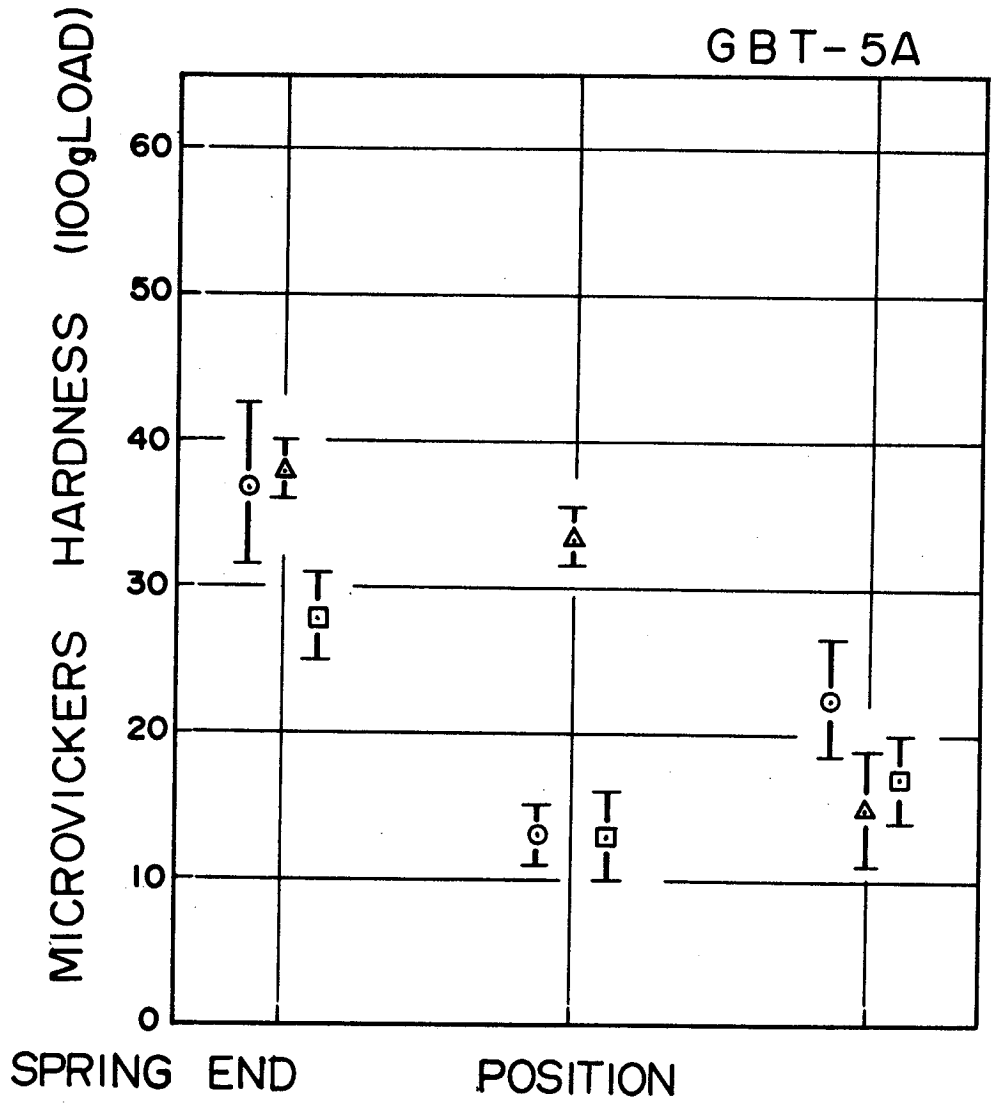


FIGURE 10A. MICROHARDNESS ON THE SECTION, SKYLAB SAMPLE 1A'



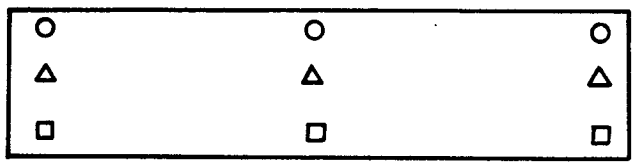
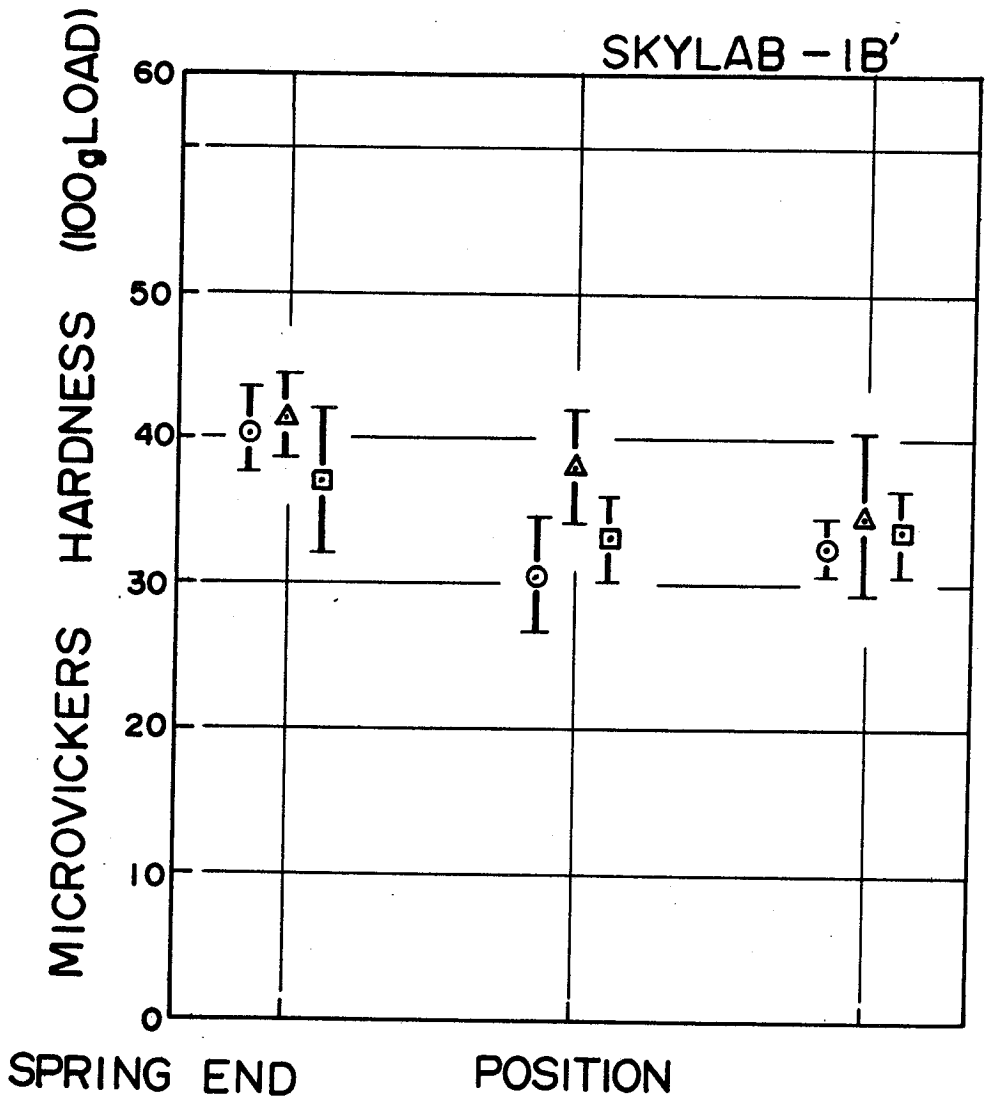


FIGURE 10B. MICROHARDNESS ON THE SECTION, GBT SAMPLE 5A



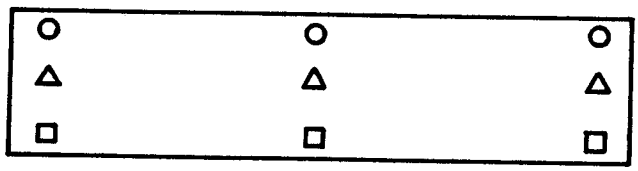
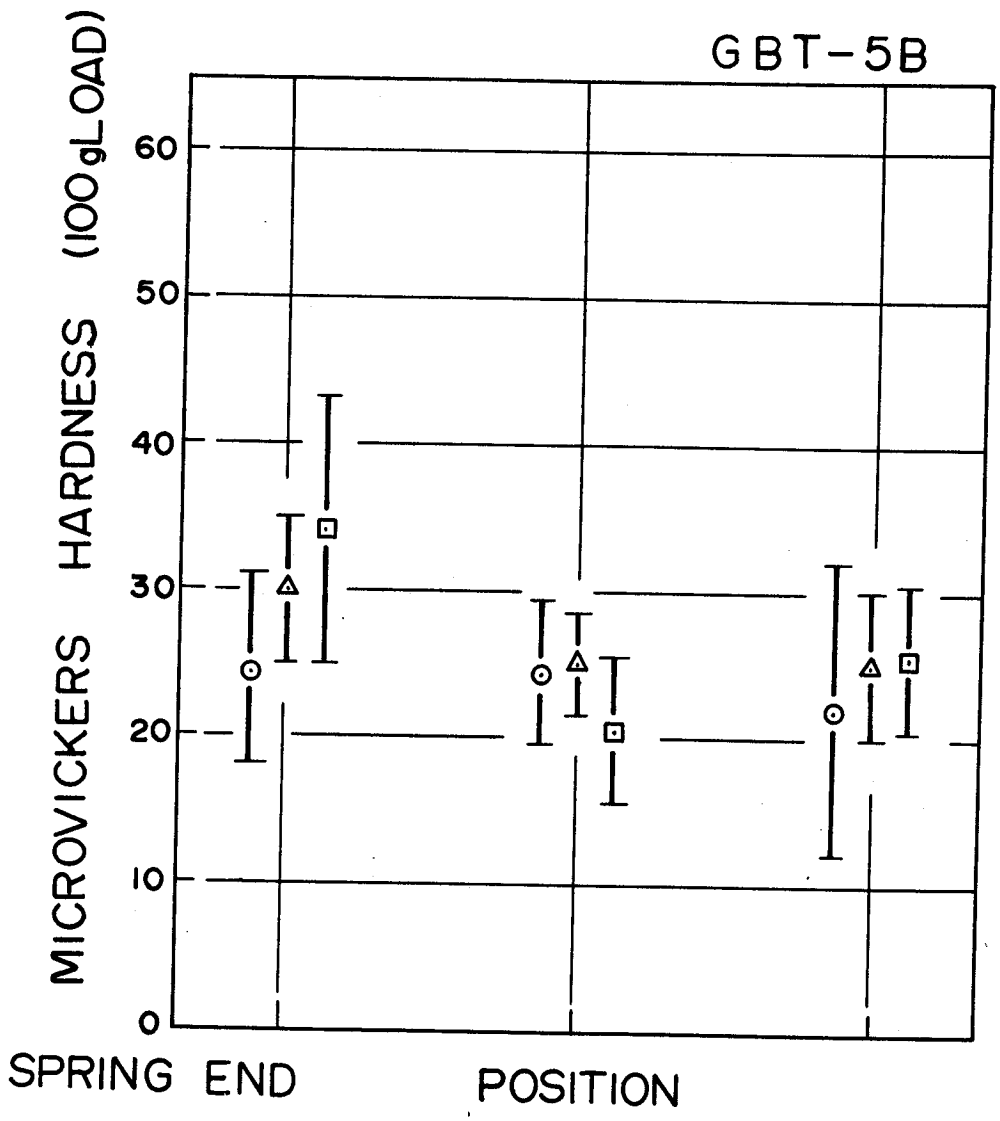


FIGURE 11A. MICROHARDNESS ON THE SECTION, SKYLAB SAMPLE 1B'



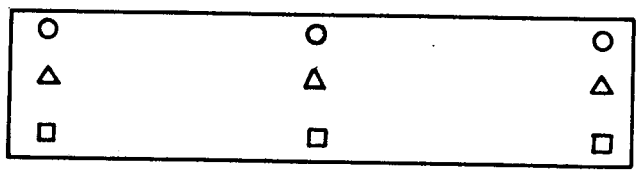
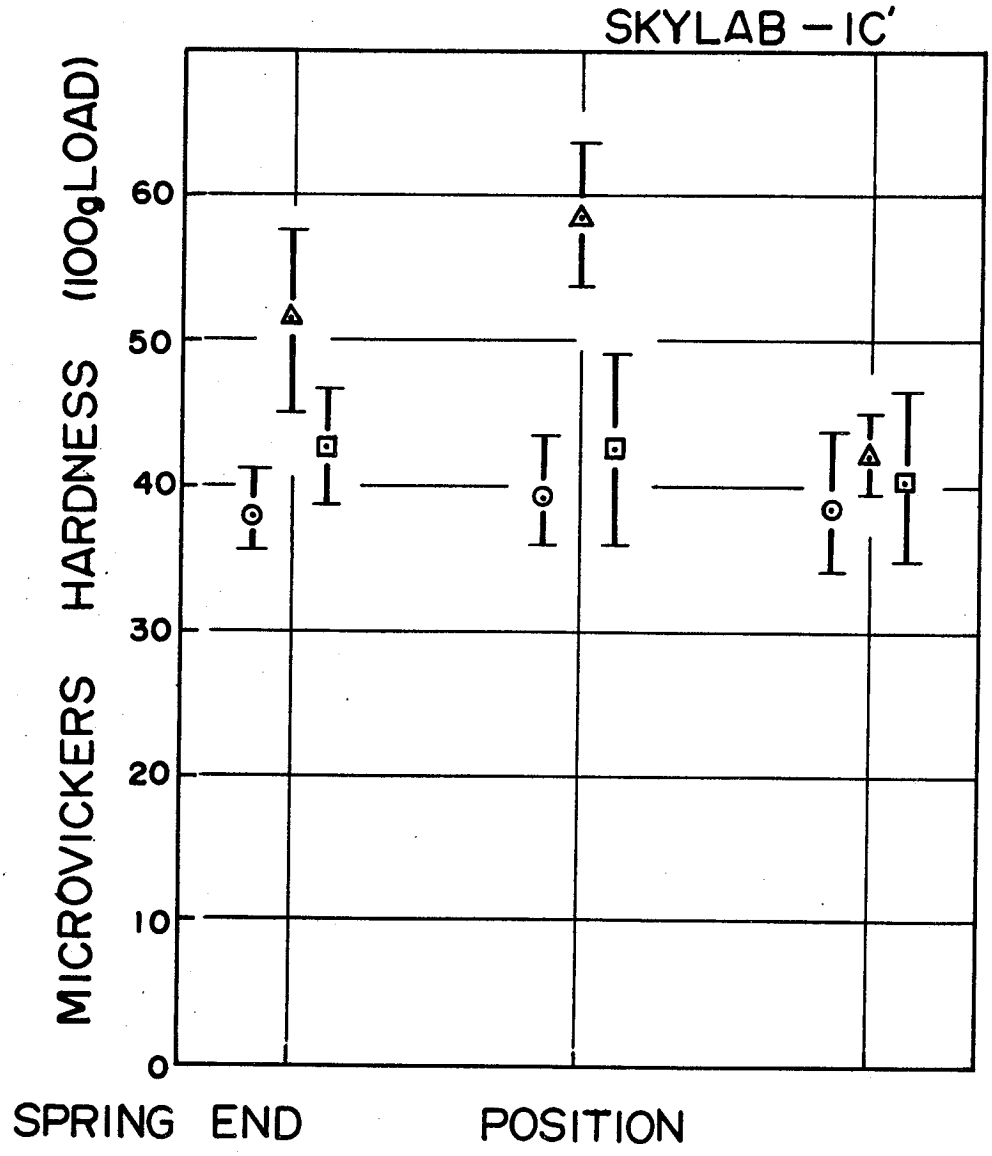


FIGURE 11B. MICROHARDNESS ON THE SECTION, GBT SAMPLE 5B



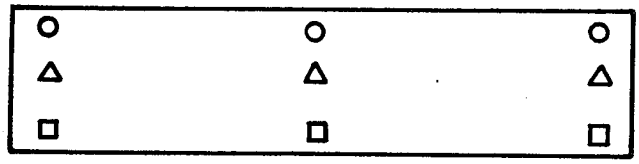
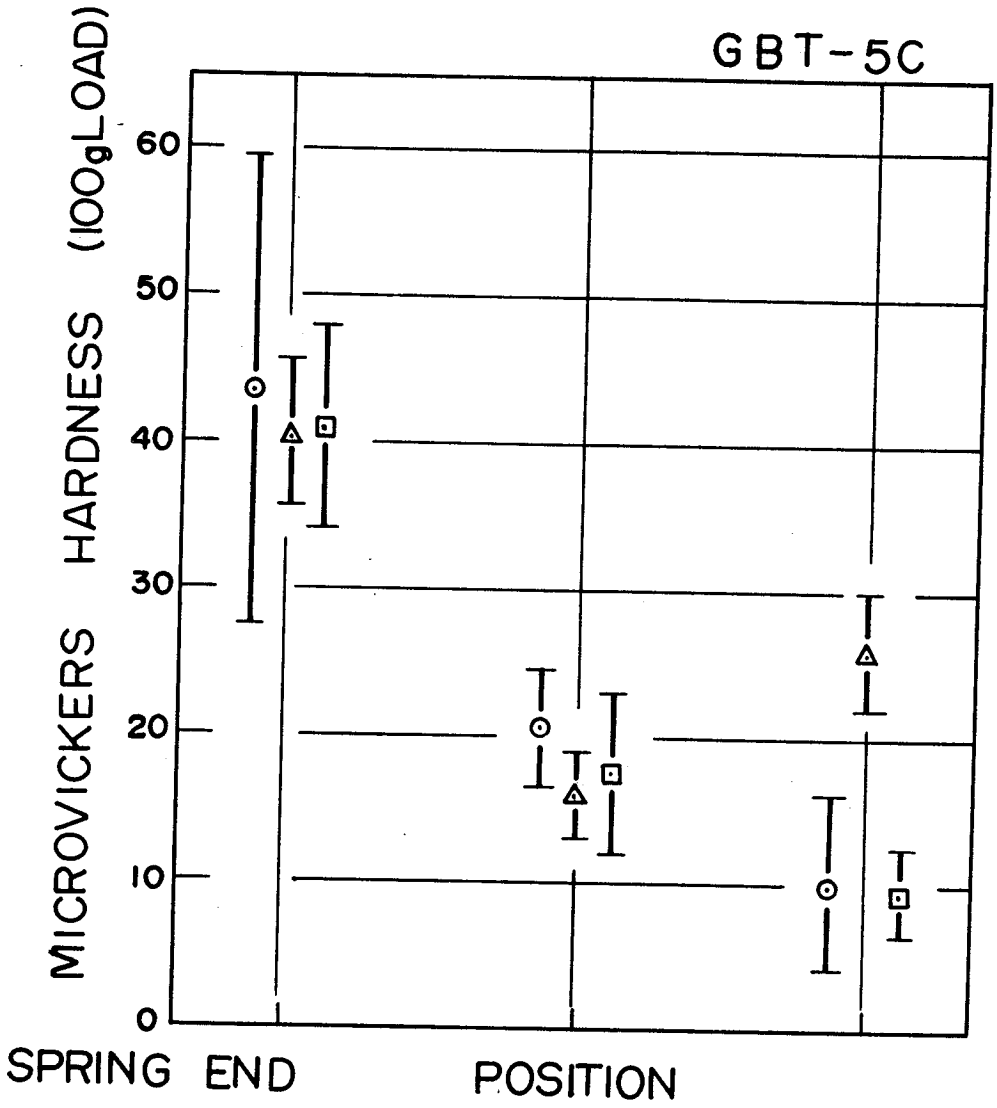


FIGURE 12A. MICROHARDNESS ON THE SECTION, SKYLAB SAMPLE 1C'



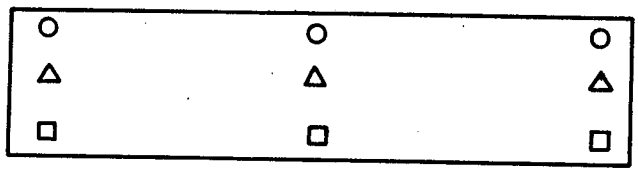


FIGURE 12B. MICROHARDNESS ON THE SECTION, GBT SAMPLE 5C

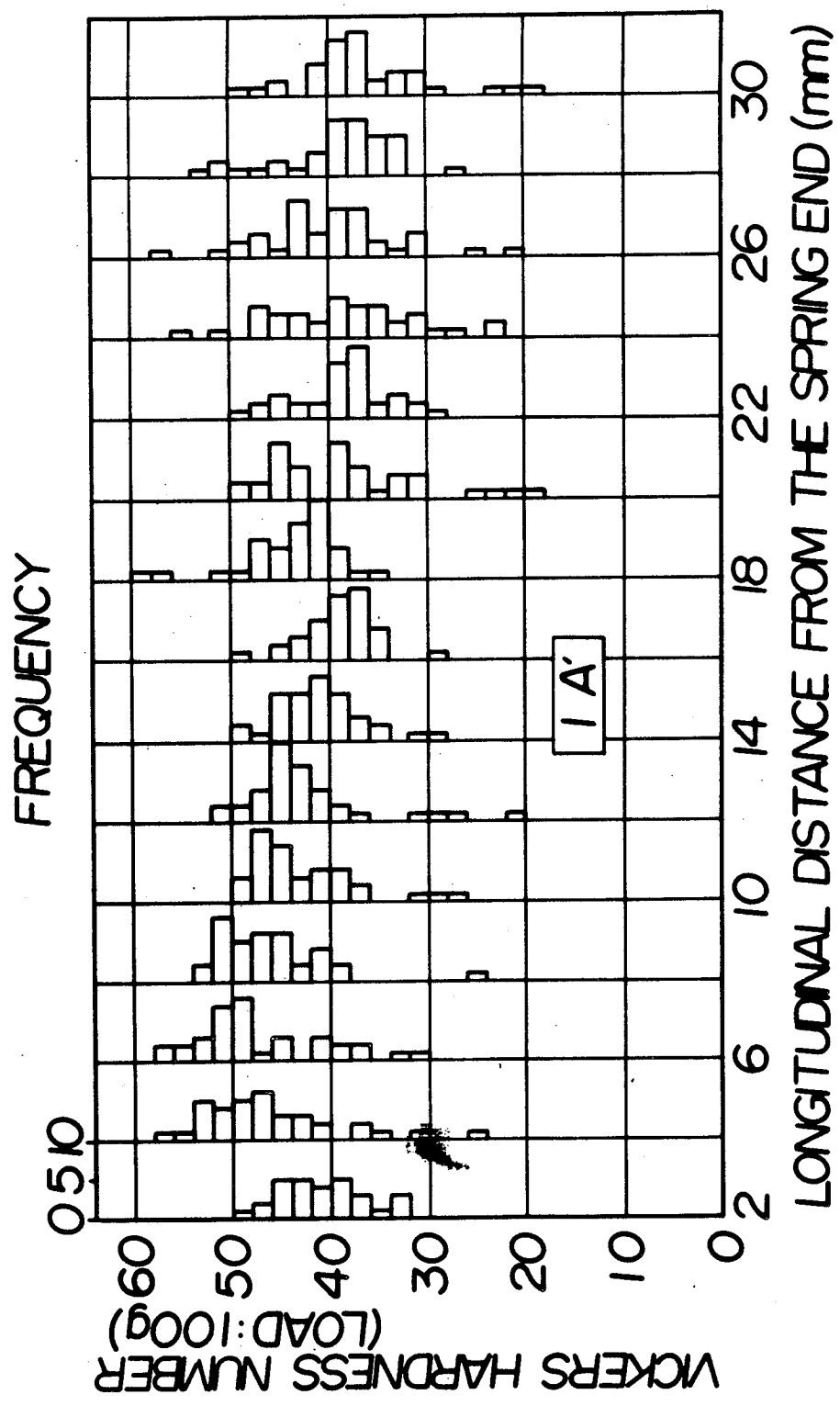


FIGURE 13A. HISTOGRAM SHOWING THE DISTRIBUTION OF HARDNESS ON THE SECTION, SKYLAB SAMPLE 1A'

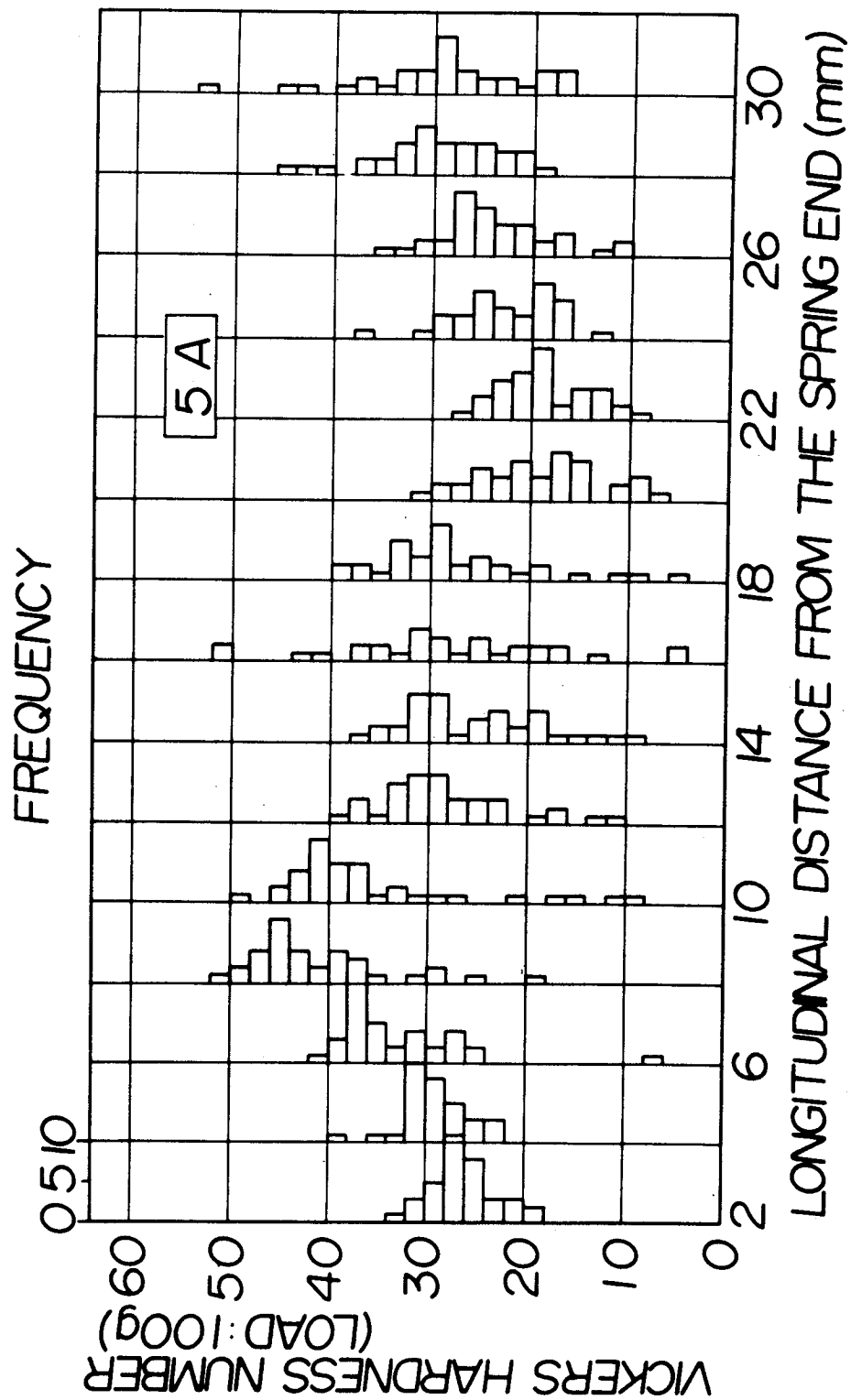


FIGURE 13B. HISTOGRAM SHOWING THE DISTRIBUTION OF HARDNESS ON THE SECTION, GBT SAMPLE 5A